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RESEARCH PAPERS

Automation of the NBS threshold photoelectron–photoion coincidence mass spectrometer

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Abstract. The pulse counting and delay circuitry for a threshold photoelectron–photoion coincidence mass spectrometer is presented along with the automation system using a DEC LSI 11/23 computer and CAMAC instrumentation. A switching output register and logic circuits are used to measure alternately a time of flight coincidence mass spectrum and a background accidental coincidence spectrum, at selected photon energies. The high voltage, fast rise time pulse used for time of flight analysis creates special signal isolation problems which are handled with unique pulse blanking techniques.

1. Introduction

As reported in review articles (see e.g. Gellender and Baker 1977, Baer 1979), many experiments in photoelectron–photoion coincidence mass spectrometry have been performed since the initial experiment by Brehm and von Puttkamer (1967). The technique of photoelectron–photoion coincidence spectrometry is the experimental method of choice in monitoring the fragmentation of parent ions as a function of their internal energy. Both thermochemical and dynamical information can be obtained directly from the coincidence experiment. Thermochemical information includes ionisation energies of molecules and appearance energies of fragment ions. Dynamical information includes unimolecular fragmentation rates as a function of parent ion internal energy and the kinetic energy released upon fragmentation. In addition, the fragmentation rates as a function of internal energy are amenable to interpretation using the quasiequilibrium theory of mass spectrometry (Rosenstock *et al* 1952).

In an effort to improve the mass resolution and data acquisition capabilities of the National Bureau of Standards coincidence apparatus, a major modification of the electronic peripherals has been undertaken. By the use of a well stabilised pulser able to provide a high voltage, fast rise time pulse ($V_{max} \simeq 500$ V, $T_{rise\ time} \simeq 8$ ns) the mass resolution has been increased from $M/(\Delta M) \simeq 35$ to $\simeq 80$. The application of such pulses leads to significant signal isolation problems which have been solved by the use of blanking and logic circuits. This has resulted in an increased ease of operation and reliability.

2. The threshold photoelectron–photoion coincidence spectrometer

The ionisation region of the NBS threshold photoelectron–photoion coincidence mass spectrometer and its associated data acquisition and processing electronics are shown schematically in figure 1. The physical design of the spectrometer has been described thoroughly in a previous publication (Stockbauer 1977). The basis of the coincidence experiment will be outlined briefly.

Dispersed ionising radiation provided by appropriate light sources and a monochromator is incident upon a gaseous sample. Photoelectrons created in the interaction region are accelerated, and analysed by a 127° sector electrostatic analyser which is set to pass those electrons originating with essentially zero kinetic energy. The threshold electron signal, normalised to light flux, and collected as a function of photon energy, constitutes the threshold electron spectrum. Alternatively, the threshold electron signal can be used to initiate a chain of events which results in an ion drawout pulse being applied to start a time of flight (TOF) mass analysis. The TOF is proportional to the square root of the charge to mass ratio of the ion. By keeping the ionisation rate sufficiently low in the coincidence experiment, the detection of a threshold electron and its coincident ion is unambiguous. Detection of many electrons and their associated ions produces a coincidence TOF mass spectrum.

The ionisation process can be represented energetically by

$$h\nu = \mathrm{IE} + E_{\mathrm{int}} + \mathrm{KE}(e^-)$$

in which $h\nu$ is the photon energy, IE is the ionisation energy, E_{int} is the parent ion internal energy, and $\mathrm{KE}(e^-)$ is the kinetic energy of the ejected electron. Since $\mathrm{KE}(e^-) \equiv 0$ in the coincidence experiment, a coincidence TOF mass spectrum recorded as a function of photon energy is a 'breakdown curve', i.e. the

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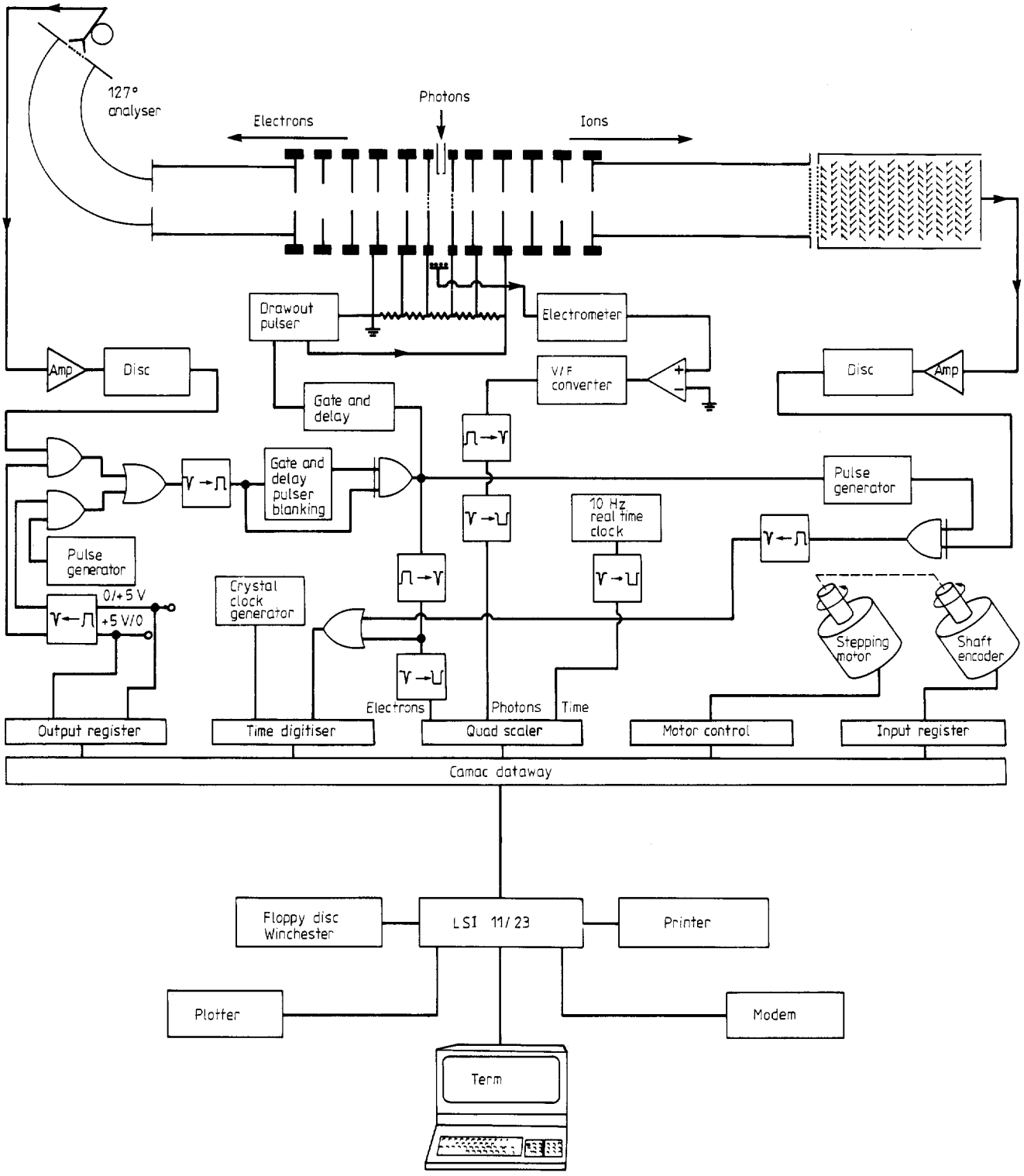

Figure 1. Data acquisition and processing electronics of the NBS threshold photoelectron–photoion coincidence spectrometer†. Fast preamplifier: Ortec, model 9301. Amplifier/discriminator: Ortec, model 9302. Constant fraction discriminator: Ortec, model 473A. Gate and delay generator: Ortec, model 416A. Universal coincidence: Ortec, model 418A. Pulse generator: Berkley Nucleonics Corporation, model 8010. Time digitiser: Joerger Enterprises. High voltage, drawout pulser: Velonex, model 360.

fragmentation of the parent ion as a function of its internal energy, $h\nu - \text{IE}$.

In the coincidence experiment the detection of a threshold electron triggers a series of events. First, it must trigger a blanking circuit to prevent a second electron or noise pulse from

† The mentioning of manufacturers is for the purpose of describing experimental detail and does not constitute endorsement of a particular manufacturer by the National Bureau of Standards or Daresbury Laboratory.

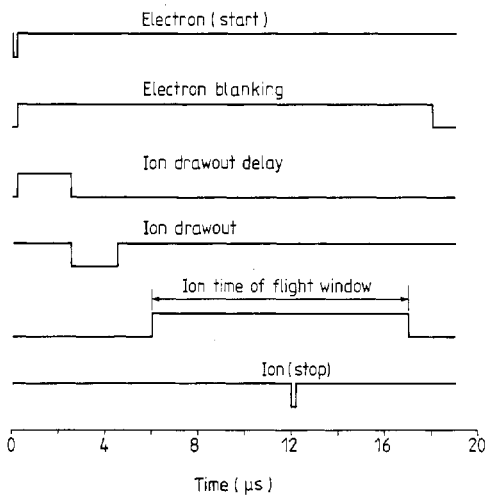

Figure 2. Relative timing of the pulses used in the acquisition of a coincidence TOF spectrum.

retripping the circuits; second, it must be counted; third, it must trigger a drawout pulse to accelerate its associated ion; fourth, it must start a timing circuit to measure the ion TOF; and fifth, it must trigger a pulse circuit to provide a TOF window for the ion. In addition, the automation allows for computer control in the acquisition of an accidental coincident background spectrum, in the scanning of the photon monochromator, in determining the photon intensity and in measuring the time during which the data are accumulated.

The pulse detection, delays, blanking and other signal processing features of the LSI 11/23 based system are shown in figure 1. The various modules require different types of signal standard (NIM, TTL or TTL complement) and these inter-conversions are performed as indicated. In the coincidence experiment, the zero kinetic energy electron is detected first. This electron signal is amplified, discriminated, and fed into one input of an AND gate. The second input of this AND gate receives a +5 V signal to turn the gate ON. A parallel AND gate is fed by an approximately 1 kHz pulse generator. This is used to simulate electron counts to enable the measurement of accidental or false ion coincidences. The outputs of both AND gates are fed into an OR gate which acts merely to deliver, indiscriminately, either the threshold electron pulse or the random pulse to the rest of the circuit. The output of the OR gate is fed into the electron gate and delay pulser blanking unit. The delayed and undelayed electron signals are inputs to a coincidence gate operating in the anticoincidence mode. This coincidence gate prevents the acceptance of another threshold electron or noise pulse before the coincident ion. The probability of detecting another threshold electron during the ion analysis time is remote ($\leqslant 1\%$). The probability of detecting a noise pulse is 100% since the electron detection circuit is sensitive enough to be triggered by the 500 V drawout pulser. Without the blanking, the triggering acts as a positive feedback circuit continually triggering the drawout pulser. The output signal from this gate serves a variety of purposes. It is:

(1) counted by a scaler;

(2) used to trigger the drawout pulser which accelerates ions out of the ionisation region;

(3) passed through an OR gate and used as the start signal to the time digitiser;

(4) used to trigger a low voltage pulse generator which provides the TOF window in which ions are collected.

The relative timing of the various pulses is shown schematically in figure 2.

The coincident ion is detected several microseconds after the threshold electron. The ion signal is amplified, discriminated, and fed into the input of an AND gate. The other input of this gate is fed by a low voltage pulse generator whose output defines the ion TOF acceptance window. This window serves the same function as the electron blanking circuit (described above). Without this acceptance window, the drawout pulse would trigger the ion detection circuit, causing the time digitiser to stop prematurely. The window provides blanking during the time in which the drawout pulser is on. The ion output of the OR gate follows the electron output in time and is used, therefore, as the stop signal to the time digitiser. The precise TOF is the time between start and stop pulses measured by the time digitiser and a crystal clock generator. If the ion TOF is greater or less than the time limits set at the beginning of the scan, the ion count is discarded. If the TOF is within the limits, a single ion event is recorded in a channel corresponding to that particular ion TOF. The computer then starts the process over again by accepting the next threshold electron. In this manner, the detection of many starts (threshold electrons) and stops (coincident ions) produces a TOF mass spectrum.

The TOF mass spectrum is accumulated until either a preset number of threshold electrons is counted or until a real time count limit is reached. This prevents the computer from dwelling at any particular photon energy for too long a time, a condition attained when the threshold photoelectron count rate is very low. At this time the counters are inhibited, read, and then

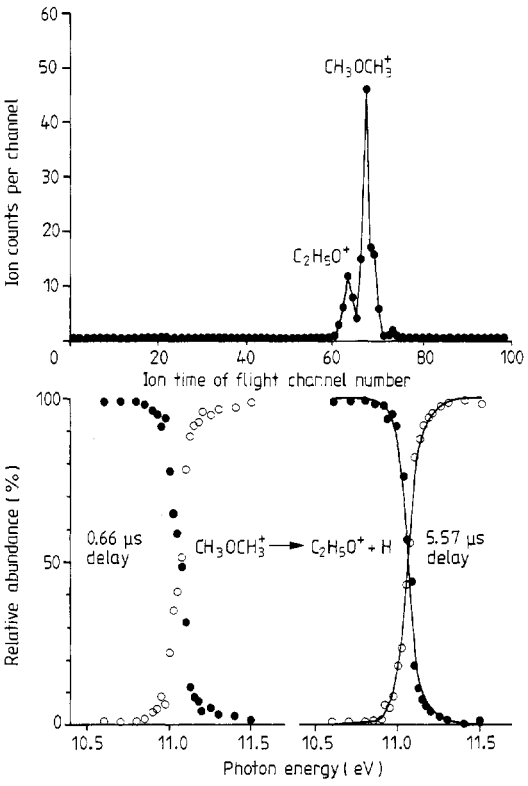

Figure 3. The upper part shows an ion TOF spectrum taken at a photon energy of 11.0 eV. The two peaks correspond to $C_2H_5O^+$ (mass 45) and the parent ion $CH_3OCH_3^+$ (mass 46). The lower part shows the breakdown curve for the dissociation $CH_3OCH_3^+$ (●) → $C_2H_5O^+$ (○) + H at 0.66 and 5.57 μs ion source residence times.

cleared by the computer. The +5 V, originally input to the AND gate which passes the real electron signal, is switched by the output register to one of the inputs of the parallel AND gate, and hence random pulses are switched into the circuit. Ions that are detected in coincidence with the random electrons constitute false coincidences or background in the TOF spectrum. The background spectrum can then be subtracted from the real coincidence spectrum. Figure 3 shows an ion TOF spectrum taken at a photon energy of 11.0 eV, together with a breakdown diagram, of dimethyl ether (Butler *et al* 1984).

In addition to a real time count limit, a photon count limit is requested by the computer in the acquisition of a threshold photoelectron spectrum. The photon intensity is proportional to the voltage output of a vibrating reed electrometer which is fed into a voltage to frequency converter and scaled.

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